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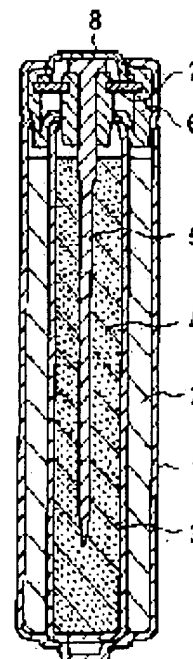
(71)Applicant : TOSHIBA BATTERY CO LTD

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YODA KIYOTO
OKAYAMA TEIJI**(54) ALKALINE BATTERY****(57)Abstract:**

PURPOSE: To provide a pollution-free alkaline battery, which generates less gas and presents less dispersion in the discharge characteristics.

CONSTITUTION: An alkaline battery comprises an alkaline electrolytic solution and a zinc negative electrode consisting in zinc powder not containing cadmium and lead, and bismuth in 0.005-0.5wt.% of zinc powder is attached to the surfaces of the zinc grains, in which a fluoric surface active agent is included in an amount 0.05wt.% or less of the zinc powder. Owing to bismuth attachment to the surfaces of the zinc powder, the filling amount of gel-form zinc negative electrode in a cylindrical separator in the battery manufacturing process does not present any dispersion, and the discharging characteristics are accordingly free of dispersion, and a pollution-free alkaline battery with less gas generation is accomplished because of the anti-corrosion effect of bismuth in the same manner as indium.

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(21)Application number : 59-251956	(71)Applicant : FUJI ELELCTROCHEM CO LTD
(22)Date of filing : 30.11.1984	(72)Inventor : SHINODA KENICHI OOTA HIROHIKO TANAKA YUZO TSUTSUI KIYOHIDE

(54) ALKALINE BATTERY

(57)Abstract:

PURPOSE: To completely eliminate or to extremely reduce the mercury content of a negative electrode zinc side by using globular zinc or globular zinc alloy which is coated and formed with an alloy layer of bismuth or bismuth and mercury as a negative electrode.

CONSTITUTION: An alloy layer of bismuth or bismuth and mercury is coated and formed on the surface of globular zinc, in which the shape of zinc particles is approximately a globe, or of globular zinc alloy which uses zinc as a main component and is containing a kind of element or more of iron, cadmium, lead, bismuth, gallium, indium, thallium, tin, magnesium and aluminium to use it as a negative electrode. Whereby, it is possible to increase hydrogen overvoltage and to highly increase the restraining effect of hydrogen gas generation and the preventing effect of corrosion, and even when completely eliminating or extremely reducing mercury, it is possible to obtain the battery performance equivalent to or in excess of the conventional battery performance.

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H01M 4/42(21)Application number : **04-129853**(71)Applicant : **MITSUI MINING & SMELTING CO LTD**(22)Date of filing : **24.04.1992**(72)Inventor : **SASAKI MASAMOTO
MOTOMURA TOMOTAKA
ASANO HIROFUMI****(54) ZINC ALLOY POWDER FOR ALKALINE BATTERY AND MANUFACTURE THEREOF****(57)Abstract:**

PURPOSE: To substantially restrain the occurrence of hydrogen gas and improve the resistance of a mercury-less alkaline battery against liquid leakage by using zinc with an extremely small content of iron as an impurity, and adding the predetermined element thereto.

CONSTITUTION: Each additional element represented by the following (1) or (2) is dissolved in the hot melt of zinc containing 1ppm or less of iron as an associated impurity to obtain the content thereof within the prescribed range; (1) 0.001 to 0.5wt.% of aluminum, and bismuth less than 0.001 to 0.01wt.%, and (2) 0.001 to 0.5wt% of aluminum, bismuth less than 0.001 to 0.01wt.% and indium equal to or less than 0.5wt.%. The product so obtained is pulverized by the atomizing method and sieved. Zinc alloy powder is thereby obtained. The occurrence of hydrogen gas can be restrained at approximately 300 μ l/day.cell or below as an upper allowable limit for leakage liquid resistance, using the zinc alloy powder.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] About the zinc-alloy powder for alkaline cells, and its manufacture method, without using the mercury and lead which are a detrimental element, by the content of the iron as a company impurity in zinc setting to 1 ppm or less in detail, and containing a specific alloying element, this invention suppresses hydrogen gas generating and relates to the zinc-alloy powder for alkaline cells which raised the liquid leakage-proof nature of a cell, and its manufacture method.

[0002]

[Description of the Prior Art] The mercury in the **ized zinc powder currently used for the negative-electrode active material of an alkaline cell suppressed generating of the hydrogen gas by zincky corrosion, and was considered to be a component indispensable to the negative-electrode active material of an alkaline cell from the purpose which prevents the liquid leakage of the cell resulting from this.

[0003] However, reduction of mercury was called for from the field of an environmental cure, and even if it made zinc reduce the content of mercury from 10 % of the weight to till around 1 % of the weight sharply lead and by adding aluminum, a bismuth, an indium, etc. as an alloying element further for this reason, it became possible to suppress generating of hydrogen gas.

[0004] However, as further social request, if the mercury content in a negative-electrode active material is put in another way 0% of the weight, considering as non-**ization is called for in recent years. Thus, it was difficult to suppress a hydrogen gas yield to predetermined level, though situations will differ sharply and the above alloying elements will be added, if a negative-electrode active material is non-**ization. That is, although the zinc-alloy powder as a negative-electrode active material which added various alloying elements from before was proposed (for example, JP,2-22984,B, JP,61-153950,A), and these could attain suppression of expected hydrogen gas generating of a mercury content even less than [1 % of the weight or it], the realization of them was not completed in non-**ization.

[0005] Moreover, the zinc corrosion depressor effect which lead has with reduction-izing of the content of mercury is recent years the most important. As for the negative-electrode active material of the low-water-flow silver alkaline cell marketed now, it is common to consist of alloy composition, such as zinc-lead, zinc-aluminum-lead, zinc-aluminum-indium-lead, and zinc-bismuth-lead. That is, it was thought that reduction-izing of a mercury content had the large place attained according to the leaden addition effect, and the non-mercuration in a negative-electrode active material could not be attained, without using lead.

[0006] Having a bad influence on a human body like [this lead] mercury is known. If the social needs which search for clean environment are taken into consideration, addition of artificial lead is not desirable. However, as mentioned above, it will set by present and, as for the unleading in a negative-electrode active material, even the case of the low-water-flow argentation will not be attained easily.

[0007] On the other hand, the attempt which suppresses generating of hydrogen gas and raises an electric discharge performance is made by reducing the content of the impurity in zinc. to JP,62-123653,A Reducing impurities, such as iron and chromium, is indicated and it sets to the 1st table the 4th page of this official report. In the negative-electrode active material using the **ized zinc-alloy powder which carries out constant-rate content of lead, an indium, and the aluminum, and contains mercury 1% of the weight, the electric discharge performance is improving by reducing iron to about 10 ppm, suppressing generating of hydrogen gas.

[0008] However, the effect that it suppressed generating of desired hydrogen gas even if a mercury content reduces the content of the iron as an impurity to about 10 ppm as mentioned above and makes alloying elements, such as lead, contain with 0% of the weight of zinc-alloy powder was not acquired.

[0009] thus, the alkaline cell which considering a negative-electrode active material as **[non-]-izing and unleading suppressed generating of hydrogen gas with fundamentally different difficulty from the case where a mercury content is low **ization of 0.6 - 1.0 % of the weight, using the zinc-alloy powder of **[non-]-izing and unleading as a negative-electrode active material, as a result raised liquid leakage-proof nature does not still have profit ****

[0010]

[Problem(s) to be Solved by the Invention] this invention was made that the technical problem of this conventional technology should be solved, and sets as the final purpose what the liquid leakage-proof nature of a non-mercury alkaline cell is raised for the purpose of offering the zinc-alloy powder for alkaline cells which suppresses hydrogen gas generating sharply, and its manufacture method in **[non-]-izing and also unleading

[0011]

[Means for Solving the Problem] Along with this purpose, wholeheartedly, this invention persons did the knowledge of the above-mentioned purpose being attained according to both synergistic effect, when the content of the iron as an impurity adds a specific alloying element to this using very few zinc as a result of research, and reached this invention.

[0012] namely, the zinc-alloy powder for non-**-ized alkaline cells of this invention -- the following -- it is characterized by the bird clapper from the zinc which contained the component by which shell selection is carried out, and contained 1 ppm or less of iron whose remainder is a company impurity (1) or 0.001 - 0.5 % of the weight of (2):(1) aluminum, bismuth 0.001 - 0.001 - 0.5 % of the weight of less than 0.01-% of the weight and (2) aluminum, less than 0.001 - 0.01 % of the weight of bismuths, and 0.5 or less % of the weight of indiums

[0013] In this invention, it is required for the content of the iron as a company impurity in zinc to be 1 ppm or less. When an iron content exceeds 1 ppm, the effect which suppresses generating of hydrogen gas is small. In 1 ppm or less of contents of iron here, below the analysis threshold value at the time of using ICP and the atomic-absorption photometry which are the usual analysis means is meant, without using separation operation with zinc and iron. Using the low zinc or the zinc-alloy powder of a content of such iron as a negative-electrode active material conventionally is not performed, and such a report is not known, either. Although it can make for a special use, for example, semiconductors, using methods, such as a zone melting, specially about the zinc metal of a high grade, it is expensive also in price and cannot be used as a raw material very for dry cells. Moreover, the example used as the end of an alloy powder is not found, either. Also in the rectification zinc made into the highest degree of purity among the zinc ingots obtained as a industrial mass-production object, the iron concentration of Japanese Industrial Standards is 20 ppm or less, among those, generally the especially low thing of impurity level of iron concentration is also 2 ppm or more. Moreover, an electrolytic zinc is also the same level.

[0014] Moreover, in this invention, the component chosen from the above (1) or (2) is contained. When the content of each component element deviates from the above-mentioned range, the problem that the effect which suppresses generating of expected hydrogen gas cannot be acquired, or a practical electric discharge performance cannot be maintained arises. The book described above even if it made alloying elements other than such a component, for example, the aluminum contained to the zinc-alloy powder used as a negative-electrode active material from before, a bismuth, calcium, etc. contain independently temporarily

[0015] Next, the manufacture method of this invention is explained. In this invention, the content of the iron as a company impurity uses zinc 1 ppm or less. As low zinc of such an iron content, the zinc ingot by the **** zinc by the electrolytic decomposition process or the vacuum distillation method is mentioned. In the former, **** zinc was fused with flux, such as an ammonium chloride, and the zinc ingot cast to mold was used as a zinc raw material of a negative-electrode active material. An iron content cannot be set to 1 ppm or less in such a zinc ingot. Although the reason removes a part for the dross which floated at the zincky melting process, it returns the zinc collected in part at the removal process to a fusion zone. It is because there is usually mixing of the iron from a decollator at this dross part removal process. Moreover, mixing of a molten-metal pump, mold, and the iron from environment is also predicted.

[0016] Each alloying element shown in the above-mentioned (1) or (2) in the molten metal of the low zinc of this iron content is dissolved so that it may become the content of the predetermined range. And next, by the atomizing method, it fine-particles-izes, it sifts out further and zinc-alloy powder is obtained. It is desirable to make the content of melting in this case and the iron in atomization atmosphere into three or less 0.009 mg/m from the standpoint of raising the depressor effect of hydrogen gas generating further. Moreover, it is also desirable from same viewpoint to carry out magnetism sorting of the obtained zinc-alloy powder.

[0017] The flow sheet which showed the difference of such a conventional method and the manufacture method of the zinc-alloy powder of this invention is shown in drawing 1.

[0018] Thus, the content of the iron in the obtained zinc-alloy powder is 1 ppm or less, as mentioned above, and this zinc-alloy powder can suppress generating of hydrogen gas below to about 300microl/day-cell (single 3 type) which is the permissible upper limit of liquid leakage-proof nature.

[0019] Conventionally, about the developmental mechanics of the hydrogen gas by zincky corrosion, the relation of the crystal structure by measurement and a guess of macroscopic capacity was only discussed, and even the generating part of gas was actually pried into and it was not solved. this invention person who thought that it would be the cause by which the technology in which it applied for that variously did not bear practical use to the non-mercury battery By performing carefully microscope observation and EPMA analysis of a generation-of-gas place When particles, such as iron as an unescapable impurity contained in zinc powder or its oxide, and an alloy, existed between zinc particles and/or in a front face, the particle traced the bird clapper to the generation source of hydrogen gas.

[0020] That is, it observed with the optical microscope that there was a specific part to which it is immersed into the electrolytic solution of an alkaline cell and the same potassium-hydroxide solution, and gas generates zinc powder continuously. next -- comparatively -- a large drop child and a narrow -- the generation-of-gas state was similarly observed using the zinc of cylindrical or a tabular And it checked that there was a place which gas generates from the same place over a long time, and the mark was given to the continuation generation-of-gas part using the sharp instrument. Next, the component analysis was performed for the above-mentioned zinc in EMPA.

[0021] Consequently, it became clear that the 0.5-5-micrometer particle which mainly contains iron is surely unevenly distributed in the continuation generating part of gas. Chromium, nickel, silver, sulfur, and oxygen were detected by the case as components other than iron. Being made when the particle of iron or an iron oxide is mainly carrying out **** minute amount mixture made the generation of gas clear from this.

[0022] As shown in Table 1, various kinds of particles which have a 0.1-several mm mean particle diameter were added so that it might become the concentration of about 1-several ppm at zinc powder or a zinc plate, and the situation of the generation of gas was observed in potassium-hydroxide solution. The result was shown in Table 1.

[0023]

[Table 1]

(各種微粒子添加によるガス発生)

添加物質	ガス発生状況
Fe_2O_3 粉	激しく連続的
Fe_3O_4 粉	激しく連続的
$\text{Fe}(\text{OH})_2$ 粉	徐々に発生
MnO_2 粉	徐々に発生
NiS 粉	徐々に発生
ステンレス片	激しく連続的
Al_2O_3 粉	発生しない
CaO 粉	発生しない
SiO_2 粉	発生しない
Fe 粉	激しく連続的
Cr 粉	徐々に発生
Ni 粉	激しく連続的

[0024] From the result of this table 1, the center and bird clapper of the generation of gas found iron, the iron oxide, and the stainless particle. Thus, as for the source of the generation of gas, a particle and it were also found by that it is mainly the particle of an iron system.

[0025] this invention person etc. rather than furthermore, the effect that the effect at the time of adding lead suppresses the simple corrosion generated between zinc and the electrolytic solution the case where the effect which suppresses the corrosion by the local battery reaction triggered with the iron which is unevenly distributed in zinc was larger, and the content of the iron as an impurity in zinc is reduced extremely -- a hydrogen gas yield -- leaden addition -- nothing -- the permissible upper limit of liquid leakage-proof nature -- lower ***** -- the knowledge also of the things was carried out

[0026] Then, in this invention, while making extremely the content of the iron as a company impurity in zinc into a minute amount, constant-rate content of the specific alloying elements other than mercury and lead is carried out. Generating of

hydrogen gas is suppressed according to both synergistic effect by this.

[0027]

[Example] Hereafter, based on an example, the example of reference, and the example of comparison, this invention is explained concretely.

[0028] In the interior of a room of 0.005 mg/m³, the iron content in examples 1-2, the examples 1-8 of reference and the example 1 of comparison - 7 atmosphere fused the electrolysis **** zinc whose iron content is 1 ppm or less at about 500 degrees C, added the specified quantity of each element shown in Table 2 at this, and created the zinc-alloy molten metal. In addition, the example 1 of comparison did not add an element.

[0029] Next, this was fine-particles-ized using direct high-pressure argon gas (blowout pressure 5 kg/cm²) in the same atmosphere, and the obtained zinc-alloy powder was sifted out to the grain size of 50-150 meshes.

[0030] Furthermore, magnetism sorting was performed using the magnet and isolation iron powder was removed. Each iron content of the obtained zinc-alloy powder was 1 ppm or less.

[0031] Here, the carboxymethyl cellulose and the sodium polyacrylate were added to what saturated the zinc oxide in potassium-hydroxide solution of 40% of concentration about 1.0% as a gelling agent, and the electrolytic solution was created.

[0032] What was mixed with 1.5g of electrolytic solutions, and gel-ized 3.0g of this zinc-alloy powder was made into negative-electrode material as it was, using the above-mentioned zinc-alloy powder as a negative-electrode active material, and the alkaline manganese dioxide cell shown in drawing 2 was created.

[0033] After carrying out the partial discharge of this alkaline manganese dioxide cell 25%, the hydrogen gas yield by the corrosion of zinc-alloy powder to generate was measured, and the obtained result was shown in Table 2. In addition, per 25% partial discharge is because hydrogen gas generating speed serves as the maximum, and carrying out a partial discharge 25% was taken as the partial discharge 25% with 1 ohm and the electric discharge conditions for 11 minutes, when the alkaline manganese dioxide cell of non-mercury was constituted and the charging time value to 0.9V was made into 100%.

[0034] The alkaline manganese dioxide cell of drawing 2 consists of the positive-electrode can 1, a positive electrode 2, a negative electrode (gel-ized zinc-alloy powder) 3, a separator 4, the obturation object 5, the negative-electrode bottom plate 6, the negative-electrode charge collector 7, a cap 8, a thermal-contraction nature resin tube 9, insulating rings 10 and 11, and a sheathing can 12.

[0035] By using as a start raw material the zinc ingot to which the content of eight to example of comparison 9 iron once cast electrolysis **** zinc 1 ppm or less as usual, the iron content fused at about 500 degrees C in the atmosphere of 5 mg/m³, added the specified quantity of each element shown in Table 2 at this, and created the zinc-alloy molten metal.

[0036] Next, this was fine-particles-ized using high-pressure argon gas (blowout pressure 5 kg/cm²) in the same atmosphere, and the obtained zinc zinc-alloy powder was sifted out to the grain size of 50-150 meshes.

[0037] Each iron content of the obtained zinc-alloy powder was 3 ppm. In addition, magnetism sorting was not performed here.

[0038] The alkaline cell shown in drawing 2 like an example 1 was created using this zinc-alloy powder, the partial discharge was performed 25%, and the hydrogen gas yield was measured. The result is shown in Table 2.

[0039]

[Table 2]

実施例等	添加元素 (w t %)			F e 含有量 (p p m)	ガス発生速度 $\mu\text{l} / \text{cell} \cdot \text{day}$
	A l	B i	I n		
実施例 1	0.01	0.002	—	≤ 1	289
実施例 2	0.01	0.002	0.05	≤ 1	121
参考例 1	0.002	0.05	—	≤ 1	186
参考例 2	0.01	0.05	—	≤ 1	116
参考例 3	0.4	0.05	—	≤ 1	252
参考例 4	0.01	0.02	—	≤ 1	157
参考例 5	0.01	0.4	—	≤ 1	230
参考例 6	0.01	0.05	0.05	≤ 1	51
参考例 7	0.01	0.05	0.4	≤ 1	110
参考例 8	0.01	0.05	0.8	≤ 1	83
比較例 1	—	—	—	≤ 1	1728
比較例 2	0.01	—	—	≤ 1	1117
比較例 3	—	0.05	—	≤ 1	581
比較例 4	—	—	0.05	≤ 1	1767
比較例 5	0.01	—	0.05	≤ 1	674
比較例 6	0.7	0.05	—	≤ 1	1331
比較例 7	0.01	0.6	—	≤ 1	580
比較例 8	0.01	0.002	—	3	781
比較例 9	0.01	0.002	0.05	3	498

[0040] As shown in Table 2, each zinc-alloy powder of the examples 1-2 in which an iron content is 1 ppm or less, and moreover has specific composition, and the examples 1-8 of reference is below about 300microl/day-cell (single 3 type) whose hydrogen gas yield is the permissible upper limit of liquid leakage-proof nature. On the other hand, although an iron content is 1 ppm or less, since, as for the zinc-alloy powder of the examples 1-7 of comparison, composition deviates from the range specified by this invention, the effect which suppresses hydrogen gas generating is not accepted. Furthermore, the zinc-alloy powder of the examples 8-9 of comparison does not ask whether since an iron content is 3 ppm, composition is included in the range specified by this invention, and the effect which suppresses hydrogen gas generating is not accepted.

[0041] To the zinc-alloy powder of the example example 1 of an experiment, and the example 8 of comparison, 1 % of the weight of mercury, it ** -ized, respectively so that it might contain 10% of the weight, and ** -ized zinc-alloy powder was obtained to it.

[0042] The alkaline cell shown in drawing 1 like an example 1 was created using this ** -ized zinc-alloy powder, the partial

discharge was performed 25%, and the hydrogen gas yield was measured. The result is plotted with the value of an example 1 and the example 8 of comparison, and is shown in drawing 3 .

[0043] As shown in this drawing 3 , when an iron content is 3 ppm, an iron content is less than the permissible upper limit of liquid leakage-proof nature irrespective of the existence of content of mercury in 1 ppm or less to a mercury content being less than the permissible upper limit of liquid leakage-proof nature at 1 % of the weight or more.

[0044] Moreover, although the examination with the same said of the zinc-alloy powder of an example 2 and the example 9 of comparison was performed, the almost same result was obtained.

[0045]

[Effect of the Invention] Above, like explanation, when the content of the iron as a company impurity dissolves zinc 1 ppm or less and a specific alloying element in a molten metal and atomizes this molten metal directly, the zinc-alloy powder for alkaline cells whose iron content is 1 ppm or less is obtained.

[0046] It can hold an electric discharge performance to the practical level while it suppresses hydrogen gas generating sharply by using for the negative-electrode active material of an alkaline cell, although this zinc-alloy powder is **[non-]izing and unleading. Moreover, since mercury and lead do not contain, the alkaline cell using this zinc-alloy powder as a negative-electrode active material also meets social needs.

[Translation done.]